Double Diffusion in Ar–N_2 Binary Gas System at the Constant Value of Temperature Gradient

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An experimental study of the "diffusion-gravitational convection" transition boundary in an Ar–N_2 binary system at different pressures and a constant temperature gradient is performed. It is shown that the diffusion is replaced by the gravitational convection at a pressure $p \approx 0.5$ MPa. In terms of the stability theory, a perturbation boundary line is determined, dividing the Rayleigh numbers plane into the regions of the diffusion and the convective mass transfer. The experimental data agree well with the theoretical values.

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1. Introduction

A spontaneous penetration of one substance into another is a phenomenon known as diffusion, which frequently occurs in nature and engineering, facilitating an equalization of the concentration gradient in a given volume. The rate of mixing depends on the heat motion of molecules; the smaller the molecular weight and the higher the temperature, the shorter the time of full mixing. More intensive mixing can be achieved with the convective mass transfer, which is implemented by force or under special conditions for flows of matter arising due to diffusion processes.

The oceanographic investigations, which were performed in the latter half of the last century, revealed "salt fountains" [1, 2] representing water regions with a sharply marked density boundary. The laboratory studies [3, 4] demonstrated that, because of temperature and salinity gradients and a slower horizontal transport of salt as compared to the heat transfer, long narrow convective cells moving alternately up and down are formed in the bulk of the liquid. This convective motion was called "double diffusive convection" [5] or gravitational convection. Double diffusive convection appears in a liquid if one condition is fulfilled: the liquid contains two or more components with different diffusion coefficients and these components should make opposite contributions to the vertical density gradient [6, 7]. Investigations of melting of ice blocks [8] and the evolution of ice coats of ponds [9] showed that, upon exposure to solar radiation, denser freshwater remains beneath thinner seawater, flowing off over some slightly sloping vertical layers formed under the mutual effect of the temperature and salinity gradients.

Studies of the thermo-effect in ternary gas mixtures revealed irregular oscillations of the temperature in the diffusion apparatus [10, 11]. Later investigations of isothermal ternary gas mixtures showed that double diffusive convection is possible not only in systems with a stable stratification of the density, but also in systems with a negative density gradient [12–15]. There are now few studies on the mechanical equilibrium instability in non-isothermal conditions. They deal with the condition of a stable stratification of the mixture density. Therefore, it seems reasonable to explore the alteration of the "non-isothermal diffusion — gravitational convection" regimes with an unstable stratification of the density in the simplest mixture, namely, a binary system. In this case, two (concentration and temperature) gradients are formed, making opposite contributions to the vertical density gradient. In this case, the conditions for the mass transfer typical of double diffusive convection are observed.

This paper reports experimental data on the processes of mixing in the Ar–N_2 binary gas system with a temperature gradient and, also, presents a theoretical analysis of the stability of the gas mixture.

2. Experiment

The experiments were performed by the two-flask method, which is widely used to determine diffusion coefficients in a wide range of temperatures and pressures [16, 17]. The two-flask installations consisted of two basic components, Fig. 1 [18].

One of the components is a gas preparation unit made up of a set of needle valves (1–10) for filling of the temperature-controlled flasks with initial gases from the high-pressure cylinders A and B, a tank (13) equalizing the pressures in the flasks, and control pressure gages (12) with special membrane dividers (11) isolating the pressure gage chamber from the volume of the flask. To avoid the effect of stray capacitances, the gas pipelines

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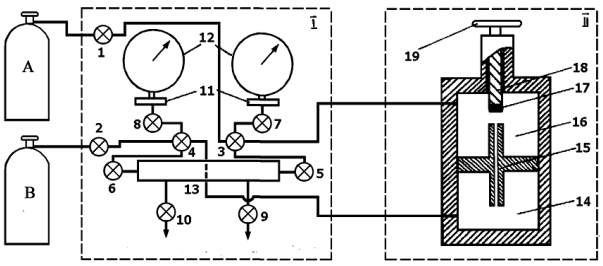

Fig. 1. Block diagram of the installation. I — gas preparation unit; II — two-flask apparatus; (1)–(10) valves; (11) membrane dividers; (12) reference pressure gages; (13) equalizing tank; (14) bottom flask; (15) diffusion capillary; (16) top flask; (17) fluoroplastic pellet; (18) rod; (19) handwheel.

were made of stainless-steel capillary tubes no more than 1.0×10^{-3} m in internal diameter, minimizing the effect of unaccounted volumes.

The second component of the installation is the diffusion apparatus itself, which is also made of stainless steel. It consisted of two temperature-controlled flasks (14, 16) with preset volumes V_{I} and V_{II} equal to 62.8×10^{-6} m^3, which were connected through a capillary (15) of radius $r = 2\times10^{-3}$ m and of length $l = 63.9\times10^{-3}$ m. In the top flask the capillary was stopped with a fluoroplastic pellet (17) attached to a rod (18), which could be advanced vertically by clockwise rotating a handwheel (19). The shut-off device was designed such that the volumes of the apparatus flasks remained unchanged at the moment the capillary was open or closed. The experiments were carried out at the change of pressure from 0.2 to 0.9 MPa and a constant value of temperature gradient. Meanwhile, the heavy gas Ar was placed in the top flask at a temperature of 283.0 ± 0.1 K, while the light gas N_2 was placed in the bottom flask at a temperature of 343.0 ± 0.1 K. A study with the top and bottom flasks of the diffusion apparatus held at a temperature of 295.0 ± 0.1 K was conducted for comparison.

The experimental procedure on the installation was as follows. The capillary between the flasks was stopped, one of the flasks was evacuated using a backing pump, then this flask was washed several times with the corresponding gas from the high-pressure cylinder, and finally it was filled with the gas to the experimental pressure. An analogous procedure was applied to the other flask. The gas pressure in the flasks of the apparatus was read against reference pressure gages (12). The absolute experimental pressure is the sum of the atmospheric pressure, which was determined by a MBP manometer--barometer, and the excess pressure read by a reference pressure gage. As soon as the installation reached the preset temperature regime, the pressure in the flasks was equalized through a special tank (13), and the excess gas was bled to the atmosphere through a valve (9). Then the capillary (15) was opened, and the experiment start time was noted simultaneously. In a certain period of time (960 s), the channel was shut-off, and the gases were analyzed in a chromatograph. The obtained experimental data were compared with the results of the calculations by the Stephen–Maxwell equations on the assumption of stable diffusion process [19]. If the experimental and theoretical values of the concentrations coincided, non--isothermal diffusion occurred in the system. If these values were considerably different, then the free convective was observed.

The experimental data are shown in Fig. 2 as the dependence of parameter $\alpha = \frac{c_{\mathrm{exp}_i}}{c_{\mathrm{theor}_i}}$ on the pressure where c_i is the concentration of diffused components. It is seen from Fig. 2 that, up to some pressure, the parameter α is on the order of unity. Hence, even with an unstable stratification of the mixture density, the conditions for molecular diffusion can be formed in this mixture. Starting from a pressure $p \approx 0.5$ MPa, the parameter α increases linearly with growing pressure. In this situation, one can suggest the presence of free convective flows, which are due to instability of the mechanical equilibrium of the mixture. It should be noted that in the case of isothermal and non-isothermal mixing, the diffusion process undergoes a transition to the convective process at the same pressure.

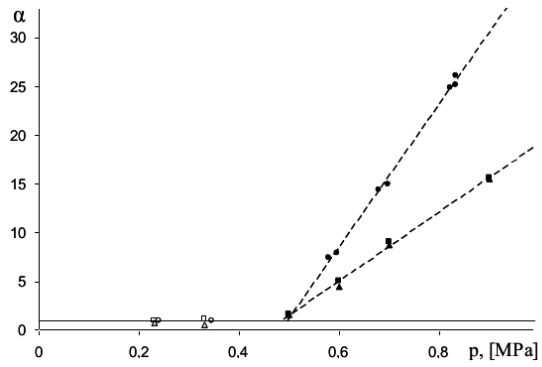

Fig. 2. Pressure dependence of the parameter α. The symbols □, ■, △, and ▲ denote the experimental data for argon and nitrogen in stable and unstable states, respectively, in the case of non-isothermal mixing. The symbols ○ and ● refer to the isothermal process. The solid line corresponds to the calculations made on the assumption of diffusion. Dashed lines are guides for eye.

As can be seen from Fig. 2, the parameter α is larger for isothermal than non-isothermal mixing. The influence of temperature gradient in the initial stage of the process (approximately ≈ 0.5 MPa) under the unstable diffusion at the isothermal and nonisothermic conditions makes no difference practically. The differences are in the limits of analysis' error of gas mixtures after the diffusion. When we further increase the pressure, while the main concentration shift happened, the transfer of components under nonisothermic conditions grows considerably in comparison with the isothermal one. That indicates the role of temperature gradient in the intensification of unsta-

ble process. Thus, the researches have shown that the intensity of unstable process increases when heating the lower flask. It is connected with the different contribution of the competitive quantities depending indirectly on the temperature to the concentration convection, viz. the diffusion coefficients (stabilizes process), the density (destabilizes process) and the mixture viscosity (stabilizes process). It seems that the density role is major.

3. Mass transfer model

The macroscopic motion of a binary gas mixture in a temperature field will be described in terms of the stability theory [20, 21]. In this case, the general set of equations of fluid dynamics consists of the Navier–Stokes equation of motion, the continuity equation, and the heat and mass transfer equations

$$\rho\left[\frac{\partial \boldsymbol{u}}{\partial t}+(\boldsymbol{u}\nabla)\,\boldsymbol{u}\right]=-\nabla p+\eta\nabla^2\boldsymbol{u}+\rho\boldsymbol{g},$$

$$\rho T\left(\frac{\partial s}{\partial t}+\boldsymbol{u}\nabla s\right)=-\mathrm{div}\boldsymbol{q}+\mu\mathrm{div}\boldsymbol{j},$$

$$\rho\left(\frac{\partial c}{\partial t}+\boldsymbol{v}\nabla c\right)=-\mathrm{div}\boldsymbol{j},\quad \frac{\partial\rho}{\partial t}+\mathrm{div}(\rho\boldsymbol{v})=0, \qquad (1)$$

where $\alpha_p=\frac{m_2-m_1}{c_1m_1+c_2m_2}$ and $\mu=\frac{\mu_1}{m_1}+\frac{\mu_2}{m_2}$.

The flow densities $\boldsymbol{j}$ and $\boldsymbol{q}$ from Eq. (1) can be expressed as the gradients of temperature, concentration, and pressure. If considerable pressure gradients are absent in the given gas mixture, we shall have

$$\boldsymbol{j}=-\rho D_{12}\left(\nabla c+\frac{k_T}{T}\nabla T\right),$$

$$\boldsymbol{q}=-\chi\nabla T+\left[\mu-\left(\frac{\partial\mu}{\partial T}\right)_{c,p}+k_T\left(\frac{\partial\mu}{\partial c}\right)_{T,p}\right]\boldsymbol{j}. \qquad (2)$$

Let us express p, c, and T as

$$p=\langle p\rangle+p',\quad c=\langle c\rangle+c',\ \text{and}\ T=\langle T\rangle+T', \qquad (3)$$

where $\langle p\rangle$, $\langle c\rangle$ and $\langle T\rangle$ are average values taken as the reference points; p', c', and T' are small perturbations. We shall assume that a change in the density, which is caused by a pressure inhomogeneity, is small as compared with the changes resulting from the temperature and composition inhomogeneities; hence, the pressure should not change considerably throughout the gas mixture; and the density ρ exhibits a linear dependence on c and T:

$$\rho=\rho_0\left(1-\beta_1T'-\beta_2c'\right), \qquad (4)$$

where $\rho_0=\rho(\langle p\rangle,\langle c\rangle,\langle T\rangle)$, β_1 is the thermal expansion coefficient of the mixture, and $\beta_2=-\frac{1}{\rho_0}\left(\frac{\partial\rho}{\partial c}\right)_{T,p}$ determines the dependence of the density on the mixture composition.

Write the variation of the mixture entropy in the form

$$\mathrm{d}s=\left(\frac{\partial s}{\partial T}\right)_{c,p}\mathrm{d}T+\left(\frac{\partial s}{\partial c}\right)_{T,p}\mathrm{d}c$$

$$=\frac{C_p}{\langle T\rangle}\mathrm{d}T-\left(\frac{\partial\mu}{\partial T}\right)_{c,p}\mathrm{d}c. \qquad (5)$$

Substituting (2)–(5) into (1), considering smallness of nonstationary perturbations, neglecting the terms quadratic in perturbations, rendering the deduced set of equations dimensionless, and taking into account that, although $\boldsymbol{u}$ and $\boldsymbol{v}$ are different in the general case, their perturbations are approximately of the same value, we shall have (the primes at the perturbed values being omitted):

$$\frac{\partial\boldsymbol{u}}{\partial t}=-\nabla p+\nabla^2\boldsymbol{u}+(R_cT+R_Tc)\,\boldsymbol{\gamma},$$

$$P\frac{\partial T}{\partial t}-(\boldsymbol{u}\cdot\boldsymbol{\gamma})=(1+a)\nabla^2T+\frac{a}{b}\nabla^2c,$$

$$P_d\frac{\partial c}{\partial t}-(\boldsymbol{u}\cdot\boldsymbol{\gamma})=\nabla^2c+b\nabla^2T,\quad \mathrm{div}\boldsymbol{u}=0, \qquad (6)$$

where r is the characteristic distance measurement scale, r^2/ν stands for the time, χ/r stands for the rate, Ar stands for the temperature; $B\chi r/D_{12}$ stands for the concentration (A is determined from the expression $\nabla T_0=-A\boldsymbol{\gamma}$; B from $\nabla c_0=-B\boldsymbol{\gamma}$); with $\rho_0\nu\chi/r^2$ being the pressure, $R_c=\frac{g\beta_1Ar^4}{\nu\chi}$ and $R_T=\frac{g\beta_2Br^4}{\nu D_{12}}$ are the Rayleigh diffusion and heat numbers, $\nu=\eta/\rho_0$, $P=\nu/\chi$, $P_d=\nu/D_{12}$, $a=\alpha^2ND_{12}/\chi$ and $b=\alpha D_{12}A/\chi B$ are the parameters characterizing thermal diffusion and diffusion heat conductivity, $\alpha=k_T/T$, $N=\left[\frac{T}{C_p}\left(\frac{\partial\mu}{\partial c}\right)_{T,p}\right]_0$ is a thermodynamic parameter (the values in square brackets are taken at average values of the temperature and the concentration). If the temperature gradient is small, the cross effects are assumed to be insignificant, i.e. $a=b=0$.

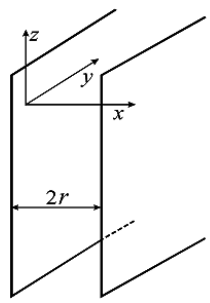

Fig. 3. Geometry of the problem. The system of coordinates.

For simplicity, the geometry of the problem is presented as an infinite flat vertical channel (Fig. 3). From geometrical considerations we shall take that the perturbations are plane-parallel, are directed along the z-axis, and depend only on one coordinate x:

$$u_x=u_y=0,\quad u_z=u(x),\quad c=c(x),\quad T=T(x).$$

It is assumed that the solution of the set (6) has the form

$$\{c,T,u\}=\left\{c^0,T^0,u^0\right\}\sin\left((n+1)\frac{\pi}{2}x\right)\exp(-\lambda t), \qquad (7)$$

where $n=1,3,5,\ldots$ are characteristic odd modes of per-

turbations. The boundary conditions suggest that the velocity and perturbations of the concentration and the temperature become zero in the vertical planes limiting the layer of the gas mixture:

$$u = c = T = 0, \quad x = \pm 1.$$

Simultaneous solution of (6) and (7) provides a cubic equation for the decrements λ,

$$p\lambda^3 + q\lambda^2 + r\lambda + s = 0, \tag{8}$$

with the coefficients $p = PP_d$, $q = -\pi^2(P + P_d + PP_d)$, $r = \pi^4(1 + P + P_d) - (PR_T + P_dR_c)$, and $s = -\pi^2(\pi^4 - R_c - R_T)$. The solution of (8) gives boundary lines of monotonic and oscillating perturbations in the form

$$R_c + R_T = \pi^4, \tag{9}$$

$$\frac{P_d^2}{1+P_d}R_c + \frac{P^2}{1+P}R_T = \pi^4(P + P_d). \tag{10}$$

Figure 4 presents a Rayleigh numbers plane with a boundary line of monotonic perturbations, MM, plotted on this plane. One can see that the boundary line MM divides the plane into two regions, namely, a region of growing perturbations above the line MM and a region of decaying perturbations below this line.

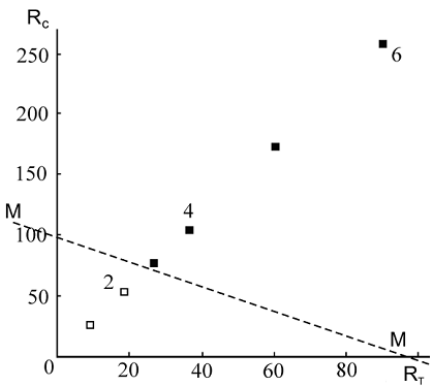

Fig. 4. Line of monotonic perturbations, MM, and the experimental data for the Ar–N_2 system on the plane (R_T, R_C). The points correspond to the pressure: (1) 0.241, (2) 0.338, (3) 0.486, (4) 0.584, (5) 0.682, (6) 0.878 MPa. $\Delta T = (60.0 \pm 0.1)$ K.

For comparison with the theoretical values, we reconstruct the experimental data as partial Rayleigh numbers. If the experimental conditions (the pressure p, the temperature and the composition contents of the mixtures in each of the flasks, the capillary dimensions r and L, and the acceleration g) are known, then from the following formulae:

$$R_c = \frac{gr^4 n \Delta m \Delta c}{\rho \nu D_{12} L} \quad \text{and} \quad R_T = \frac{gr^4 n \frac{\bar{m}}{T} \Delta T}{\rho \nu \chi L}, \tag{11}$$

it is possible to determine the point in the Rayleigh numbers plane, which the given experiment reflects. Here $n = \frac{p}{kT}$, $\Delta m = m_1 - m_2$ is the difference between the molecular masses of the first and second components, $\Delta c = c_{\mathrm{I}} - c_{\mathrm{II}}$ is the difference between the concentrations of the selected component in the top and bottom flasks, $\Delta T = T_{\mathrm{I}} - T_{\mathrm{II}}$ is the difference between the temperatures of the diffusion apparatus flasks, and $\bar{m} = c_1 m_1 + c_2 m_2$.

The symbols in Fig. 4 correspond to the experimental data for the Ar–N_2 mixture, when the transition from the state of stable diffusion to the unstable range occurs subject to the pressure and at the constant temperature gradient. The open and full symbols denote diffusion and convection, respectively.

In accordance with the experimental data presented in Fig. 4, the unstable regime occurs as from ≈ 0.5 MPa. Point 3 corresponding to the given experimental conditions is situated close to the boundary line MM. Further increase of pressure (points 4, 5 and 6) shows that all points representing the experiment are in the area where the convective mechanism operates. The experimental data on mixing in theAr–N_2 system presented in Fig. 2 agree with the experimental results, regarding the stability boundary.

4. Conclusions

The study is performed with the aim to determine the boundary of transition in a binary mixture of Ar–N_2 with an unstable stratification of the density in the presence of a temperature gradient. It is shown experimentally that two mixing regimes, namely, the diffusion and the convective mass transfer occur in the binary system with the unstable stratification of the density. The transition between the two regimes takes place at the pressure $p = 0.5$ MPa. The experimental data are in good agreement with the theoretical results obtained in terms of the linear theory of stability.

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